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(54) Title: RECYCLING OF FIBRE PRODUCTS

(57) Abstract

In a method of recycling printed paper, the collector chemical used to aid ink removal after pulping of the paper, comprises a saponaceous product formed by reaction of a long-chain fatty acid, for example tall oil, and an amine, for example triethanolamine. Such a product is suitably liquid at ambient temperatures, and so is convenient for transportation and use. It is highly active. Also described is a dispersant, an ester derived from an ethylene oxide/propylene oxide co-polymer, and a long-chain fatty acid. Co-use of such a dispersant with the collector chemical appears to enhance its utility.

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RECYCLING OF FIBRE PRODUCTS

This invention relates to a method of recycling fibre products, namely printed paper products. The invention 5 relates in particular to a method of recycling fibre products involving subjecting them to a mechanical treatment to separate fibres, removing the ink therefrom (commonly known as "deinking"), and recovering the fibres.

10 The recycling of paper products is now an important industry. Initially, paper products, particularly for the box and board industry, were recycled without deinking. A later development was the use of waste paper as a source 15 of fibres for the production of newsprint but now certain waste paper products can be deinked, and used for higher quality papers, for example tissue, cartridge and writing papers.

A common method of paper recycling is to subject 20 waste paper to a mechanical pulping treatment to break the paper down into fibres in an aqueous medium, and then to use a flotation technique to remove ink, followed by a washing treatment. To remove the ink, a chemical, commonly referred to as a collector chemical, is present, 25 and air is introduced at the bottom of the flotation chamber. The air, in the presence of the collector chemical, transports ink to the surface of the aqueous medium. At the surface, the ink-rich foam is removed by mechanical means.

30 The collector chemical is an essential component, in assisting the transport of ink to the surface and trapping the ink in a stable foam at the surface. Thus, the collector chemical must, of course, cause the ink 35 particles to be taken up efficiently and form a

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sufficiently stable foam but there are other requirements to be borne in mind. For example, if solid, it should dissolve readily; if liquid, it should be easy to handle; it must be safe; it should be inexpensive to use; it 5 should be easy to transport; and so forth.

The fatty acid soaps of alkali metals, for example sodium or potassium, are widely used as collector chemicals.

10

To saponify in situ requires a relatively high pH. However, the higher the pH in the fibre pulp, the greater the risk of fibre damage. Furthermore, the subsequent process of paper making is an acid process, so the more 15 alkaline the aqueous medium in the deinking chamber is, the more acid is required in the subsequent paper-making process. It must also be borne in mind that there is a certain degree of hysteresis in the matter of pH of solutions containing paper pulp because of the absorption 20 of alkaline or acid moieties within fibres.

To saponify to form a fatty acid soap of an alkali metal just before introduction into the deinking chamber requires extra equipment, in the form of a saponification 25 plant at the paper mill, and an extra step.

The fatty acids are available in a liquid form, either as hot molten fatty acids or in aqueous emulsion. A disadvantage of the former is in their transportation 30 and disadvantages of the latter are that aqueous emulsions at most contain only 30% active material, and there can be problems of emulsifier build up. So, in both cases there is a penalty in terms of transportation costs.

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A very small part of the market for collector chemicals is taken by synthetic detergents, for example ethoxylates, which are not derived from fatty acids. However, such detergents have not been found to be very
5 efficient for the flotation process.

A third approach, which is more common than the approach of using synthetic detergents, but less common than the approach of using fatty acids saponified in situ
10 or just before introduction into the deinking chamber, is to use alkali metal soaps of long-chain fatty acids, transported as soaps to the paper recycling plant. However, such soaps are naturally solid materials and have to be dissolved in situ or before introduction into the
15 deinking chamber. Even though the soaps are available in pelletized form, there can be a problem since dissolution can still be slow. To avoid this problem, the soaps can be supplied in aqueous solution, but only to a maximum 30 wt% of the soap in the solution. So, again there is a
20 penalty in terms of transportation cost.

Another method of paper recycling is the wash deinking process in which the substantially broken-down paper products are washed, without gas being employed to
25 carry ink particles to the surface. Instead, ink removed from the paper products is extracted on removal of the aqueous medium, for example by a draining step. A collector chemical is present to aid the removal of the ink from the paper products. Typically, a wash deinking process employs several cycles of dilution, washing and water removal and/or rinsing.
30

Dual methods of paper recycling, involving flotation deinking and wash deinking, are also employed, especially
35 in Japan.

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In accordance with a first aspect of the present invention there is provided a method of removing ink from paper products, comprising providing an aqueous medium which contains paper fibres derived from the paper products, in substantially broken-down form, and which also contains a collector chemical, characterised in that the collector chemical comprises a salt formed by reaction of a long-chain fatty acid, and an amine of general formula $R^1R^2R^3N$, wherein R^1 represents a group of general formula $-C_nH_{2n+1}$ or $-C_n(OH)H_{2n}$, where n represents an integer from 1 to 6 inclusive, R^2 represents a hydrogen atom or a group of general formula $-C_mH_{2m+1}$ or $-C_m(OH)H_{2m}$, where m represents an integer from 1 to 6 inclusive, and R^3 represents a hydrogen atom or a group of general formula $-C_pH_{2p+1}$ or $-C_p(OH)H_{2p}$, where p represents an integer from 1 to 6 inclusive.

* In a flotation deinking method, it is convenient, but not essential, that the gas passed through the aqueous medium is air.

The use of a salt formed by reaction of an amine and a long-chain fatty acid may ameliorate many of the problems encountered with prior art methods. Although salts formed by reaction of certain amines and certain long-chain fatty acids may be solid materials at room temperature (and it should be noted that the use of such materials is within the scope of the present invention in its broadest aspect), certain such reaction products are liquids, or else have a melting point sufficiently close to normal ambient temperatures that they may be made liquid by addition of appropriate fluidising agents.

Preferred salts formed by reaction of amines and long-chain fatty acids used in the present invention are

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liquid at normal temperatures of use and transportation, for example in the range 5-25°C, or are components of compositions which are liquid within that temperature range (for example being liquifiable by addition of 5 relatively minor amounts of fluidising agent(s)). Such salt reaction products of amines and long-chain fatty acids are preferred for use in the method of the present invention because they are readily transportable in high concentration, up to 100% for certain examples which are 10 liquid without the requirement of a fluidising component, or at least 50%, preferably at least 75%, and most preferably at least 90% by weight of total composition for other examples. Thus, such collector materials have the advantage of being pre-manufactured saponaceous materials, 15 which do not have to be dissolved to form a liquid composition on site. Preliminary experimental tests have shown that the efficiency of such saponaceous products in the removal of ink from fibre products is high.

20 A fluidising agent, when present, may suitably be selected from a polyhydric alcohol or a polyoxyalkylene glycol. Examples of suitably polyhydric alcohols are alkylene glycols, for example C₁₋₈ alkylene glycols, for example ethylene glycol and hexylene glycol, glycerol, 25 polyalkylene glycols, for example polyethylene glycol, and the series of polyhydric alcohols available from Shell under the Trade Mark DOBANOL. Examples of suitable polyoxyalkylene glycols are polyethylene oxide glycol, polypropylene oxide glycol and the copolymers thereof. 30 Preferably, the fluidiser component, when present, is a polyhydric alcohol, especially a C₁₋₈ alkylene glycol, most preferably hexylene glycol.

35 The amine may comprise a primary and/or a secondary and/or, most preferably, a tertiary amine.

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Suitably, the amine is of general formula $R^1R^2R^3N$ wherein R^1 represents a group of general formula $-C_n(OH)H_{2n}$, where n represents an integer from 1 to 6 inclusive, R^2 represents a hydrogen atom or a C_{1-6} alkyl group or a group 5 of general formula $-C_m(OH)H_{2m}$, where m represents an integer from 1 to 6 inclusive, and R^3 represents a hydrogen atom or a C_{1-6} alkyl group or a group of general formula $-C_p(OH)H_{2p}$, where p represents an integer from 1 to 6 inclusive. Preferably, hydroxyalkyl or alkyl groups R^1 10 and/or R^2 and/or R^3 is/are straight chain, and a hydroxy group is terminal in the respective chain.

Preferably, R^1 represents a straight chain group of general formula $-C_nH_{2n}-OH$ where n represents an integer of 15 from 1 to 4 inclusive, R^2 represents a hydrogen atom or, more preferably, a straight chain group of general formula $-C_mH_{m+1}$ or $-C_mH_{2m}-OH$ where m represents an integer of from 1 to 4 inclusive, and R^3 represents a hydrogen atom or, more preferably, a straight chain group of general formula 20 $-C_pH_{2p+1}$ or $-C_pH_{2p}-OH$ where p represents an integer of from 1 to 4 inclusive. Suitably, each of symbols n , m and p represents the integer 1 or, more preferably 2. The amine may suitably be a monoalkanolamine, dialkanolamine or trialkanolamine, for example monoethanolamine, 25 diethanolamine or triethanolamine. Suitably, the amine comprises a trialkanolamine, preferably triethanolamine, preferably substantially solely or in major proportion. For example a commercially available composition comprising 85 wt% of triethanolamine and 15 wt% of a 30 mixture of amines, predominantly diethanolamine and monoethanolamine, may suitably be employed.

Suitable long-chain fatty acids may readily be selected, forming soaps with the amines which are useful 35 in the method. Typically, such long-chain fatty acids may

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be C₁₂₋₂₂ fatty acids, or fatty acids having equivalent properties, for example C_{24:4} dicarboxy fatty acids, effectively dimers of C₁₂₋₂₂ monocarboxy fatty acids.

5 Those skilled in the art will be aware of the very wide range of fatty acids which would lend themselves to use in the method of the present invention. Preferably, though not essentially, a fatty acid is selected, which provides a salt reaction product with the amine selected
10 which is liquid at normal temperatures of use, or which can be made liquid by addition of an appropriate fluidiser component, as referred to more fully above. Examples of suitably fatty acids may include saturated fatty acids, mono-unsaturated fatty acids, di-unsaturated fatty acids
15 and tri- unsaturated fatty acids, fatty acids with hydroxy groups in the molecule, and cyclic fatty acids. It will be appreciated by those skilled in the art that the commercially available fatty acids of this type will typically comprise a mixture of different fatty acids most
20 of which are within the definition C₁₂₋₂₂ fatty acid. Examples of individual fatty acids of this type include lauric acid, myristic acid, palmitic acid, stearic acid, palmitoleic acid, oleic acid, linoleic acid, linolenic acid, arachidic acid and erucic acid.
25

The preferred commercially available fatty acids are characterised by a high degree of unsaturation.

30 In relation to the relative proportions of the amine, the long-chain fatty acid and the fluidiser component, when present, the amine and the long-chain fatty acids are desirably present in approximately stoichiometric proportion. The fluidiser component, when present, is desirably present in small quantity relative to the other
35 two components. For example the fluidiser component may

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be present as 0-10% by weight based on the total weight of the composition.

The preparation of a saponaceous reaction product which is liquid at normal ambient temperatures, which is a preferred composition for use in the method of the present invention, may simply be prepared, in many cases, by mixing the amine and the fatty acid, suitably at ambient temperature, and adding, at any convenient stage, a fluidiser component, if required. The conditions may be selected by the skilled man, using trial and error and analysis of the reaction products if necessary, to provide that a salt is the primary product formed, rather than an ester (from a tertiary amine) or an amide or ester (from a primary or secondary amine). It should be noted that in accordance with the present invention, a salt should be the major product, if it is not the only product. Thus, minor quantities of covalent reaction products can be tolerated.

20

The method in accordance with the invention may for example be a flotation deinking method, or a wash deinking method, or a dual method. The method may be of particular benefit in relation to flotation deinking. The collector chemical may advantageously be used in association with a dispersant. This may be of particular benefit in permitting the said collector chemical to be used with advantage in a wash deinking method of removing ink from paper products. It may also enhance the effect of the collector chemical in a flotation deinking method, to a substantial and surprising degree. The said collector chemical and the said dispersant, when present, may be components of a single composition, preferably liquid, added together, preferably at the deinking stage, otherwise at the pulping stage. However, preliminary

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tests have indicated that there may be advantages in adding the dispersant at the pulping stage, and adding the collector chemical subsequently, at the deinking stage.

5 Any dispersant effective to aid the dispersion and/or dissolution of ink removed from the paper products by the collector chemical, to the extent that on removal of aqueous medium effective co-removal of ink from the washing bath in a wash deinking process is achieved, may
10 be employed. Examples may include alkoxylates, for example alkylphenol ethoxylates, alcohol ethoxylates, amine ethoxylates, ester ethoxylates, acid ethoxylates; sulphonates, for example alkylaryl sulphonates, alkane sulphonates; and esters of alkylene oxide polymers. A
15 preferred dispersant is an ester derived from an ethylene oxide/propylene oxide co-polymer (preferably of molecular weight in the range about 600 to 3000), and a C₁₂₋₂₂ fatty acid, for example stearic or tallow fatty acid. In such a preferred dispersant composition an alkyl aryl
20 sulphonate may desirably be present to modify the dispersant properties, and if so it is desirable for reasons of stability of the dispersant composition, to terminate the esterification leaving a moderate concentration of unreacted fatty acids. In such a dispersant composition the ester component is suitably a major component and the sulphonate component a minor component, and the acid number of the ester component (the percentage by weight of free fatty acids present, measured
25 in accordance with test BS 684 1958) is desirably about 2-8, preferably about 3-5.

Suitable alkyl aryl sulphonates have a long-chain (eg. C₁₂) alkyl group. Preferred such sulphonates are alkyl benzene sulphonates and alkyl xylene sulphonates.

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Preferably, the dispersant, when present, is itself a liquid at ambient temperature.

Suitably, the dispersant may be present in an amount 5 of from about 0.01 to about 1%, by weight of dry waste paper, preferably from about 0.05 to 0.5%, most preferably about 0.07 to 0.15%.

The optimal weight ratios of collector chemical to 10 dispersant, when present, will depend on the exact nature of the particular deinking process employed and on the nature of the paper and the ink printed thereon. Trial and error may easily be used to determine the optimal proportions in any given case. Typically, the weight 15 ratios could be in the range 95:5 to 5:95, (collector chemical:dispersant). It is believed that higher collector chemical: dispersant ratios (for example 80:20 by weight) may be preferred for newsprint and other coarse papers, containing lignin and hemicelluloses in 20 substantial quantity, whilst lower ratios (for example 20:80 by weight) may be preferred for higher quality, so-called "woodfree" papers.

In accordance with a further aspect of the present 25 invention there is provided any novel collector chemical or collector chemical composition which is herein described or defined.

A further aspect of the present invention is provided 30 by a composition comprising a collector chemical of the type defined herein and a dispersant, preferably an ester of an ethylene oxide/propylene oxide co-polymer and a fatty acid, as described above.

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In accordance with a further aspect of the present invention there is provided a method of recycling printed paper products, comprising: subjecting the paper products to a mechanical treatment (pulping) in an aqueous medium
5 until substantially broken down into fibres; adding to the medium, before, during or after the mechanical treatment, a collector chemical; passing a gas through the aqueous medium containing the fibres and the collector chemical and removing the ink-rich foam on the surface and/or
10 removing ink by successive cycles of draining and rinsing; and recovering the cleansed paper pulp; characterised in that the collector chemical is the reaction product of an amine as defined above and a long-chain fatty acid as defined above.

15

Preferably, the collector chemical is present in an amount from about 0.01 to about 2 wt%, for example from about 0.05 wt% to about 2 wt%, preferably from about 0.1 to about 1 wt%, most preferably from about 0.15 wt% to
20 about 0.5 wt%, based on weight of dry waste paper. The collector chemical can be added to the aqueous medium before, during, or after the completion of the mechanical treatment. Preferably it is added after the completion of the mechanical treatment, at the deinking stage, most
25 preferably shortly before or substantially at the commencement of ink removal.

It may be desirable to employ products such as sodium hydroxide, sodium silicate and hydrogen peroxide in the pulping and/or deinking steps, as is standard.
30

The invention will now be further described, by way of example.

35 Example 1

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A saponaceous material which is liquid at ambient temperature was prepared from the following materials:

- untreated tall oil fatty acids (TOFA) with a maximum rosin content of 2 wt% : 63.4 wt%

5 - 85 wt% triethanolamine with 15 wt% of a mixture of amines, including diethanolamine and monoethanolamine : 31.6 wt%

- hexylene glycol : 5 wt%

10 The alkanolamine was added slowly with stirring to the tall oil fatty acids and stirred well for a further 15 minutes. After this period of stirring, the hexylene glycol was added in one batch and the reaction mixture stirred for a further 5 minutes. The liquid amine soap 15 thus prepared, of appearance a clear red or brown liquid showing a pH (5% aqueous) of 7.0 to 9.5 was then ready for use in the deinking of paper. The formation of the amine salt was confirmed by infra-red spectroscopy.

20 Deinking tests took place in a standard laboratory flotation cell. The waste paper previously pulped to mechanically break down the paper substantially into fibres was added to the flotation cell in standard dilution in water. The liquid soap was added in one batch 25 at the rate of 0.25 wt% based on the weight of the dry paper.

The flotation cell was started and allowed to run for 45 minutes at 45°C and an air flow of 2 litres/minute.

30 The efficiency of the process was assessed by measuring the brightness of the pulp before entering the flotation cell which was 48.6 and the brightness of the pulp leaving the flotation cell after deinking which was 35 61.8. The brightness was measured on a standard PHOTOVOLT

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reflectance meter. The result was regarded as satisfactory.

Example 2

5 A liquid dispersant composition was prepared by heating together an ethylene oxide/propylene oxide random co-polymer (87 wt%) (EMKAROX VG 127W, Trade Mark, ICI Chemicals; RMM is c.1200) and distilled tallow fatty acids (13 wt%). The mixture was heated at 240°C at atmospheric
10 pressure (in an alternative preparation, at 160°C in the presence of butyl titanate catalyst) until the free fatty acid value, determined by the test BS 684 1958, fell to 4.0 (approximately 6 hours). To the reaction product (80 wt%), itself effective as a dispersant, was added a C₁₂
15 alkyl benzene sulphonate (20 wt%).

Example 3

20 A composition suitable for use in a flotation deinking process or especially, in a wash deinking process, was prepared by adding the collector chemical of Example 1 (90 wt%) to the dispersant composition of Example 2 (10 wt%).

25 Example 4

A further composition was prepared by adding the collector chemical of Example 1 (80 wt%) to the dispersant composition of Example 2 (20 wt%).

30 With this composition, in laboratory flotation deinking trials, in which the composition was added to the flotation cell not the pulper, with a variety of printed papers being treated, consistent brightness gains were
35 observed, of between 10 and 13 points (treated pulp cf.

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untreated pulp), as measured using the PHOTOVOLT reflectance meter.

Example 5

5

A further composition was prepared by adding the collector chemical of Example 1 (20 wt%) to the dispersant composition of Example 2 (80 wt%).

10

With this composition, in a laboratory flotation deinking trial, with the composition being added to the pulper not the flotation cell, a brightness gain of 16 points was achieved, as measured using the PHOTOVOLT reflectance meter.

15

Example 6

In other trials 0.08% on weight of dry paper, of the product of Example 2, was added at the pulping stage. 20 Then 0.02% on weight of dry paper, of the product of Example 1, was added after pulping, at the deinking stage. This gave excellent results, which appear to be better than results, themselves good, achieved by adding 0.1% on weight of dry paper, of the pre-mixed product, at the 25 pulper stage.

It will be appreciated that the terms "paper" and "paper products" have been widely used in this specification as shorthand terms for cellulose fibre mats wet laid by a non-woven process and is intended to include materials such as tissue, card and the like.

It is conventional in the art to state that the mechanical treatment of waste paper breaks the paper down 35 in "fibres". That conventional terminology has been used

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in this specification. It will be appreciated that such "fibres" of broken-down paper may themselves comprise smaller fibrils, and that the method of the invention does not require that the waste paper be broken down into
5 discrete, individual cellulose strands.

The terms "ink", "print" and "deinking" etc. are used herein in a broad sense to denote marking on paper, however produced, including by, for example, photocopying
10 where it might otherwise strictly be said that the marking applied is not "ink", nor is applied by conventional "printing".

15 The reader's attention is directed to all papers and documents which are filed concurrently with this specification, and which are open to public inspection with this specification and the contents of all such papers and documents are incorporated herein by reference.

20 All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features
25 and/or steps are mutually exclusive.

Each feature disclosed in the specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving
30 the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

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The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

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CLAIMS

1. A method of removing ink from paper products, comprising providing an aqueous medium which contains paper fibres derived from the paper products, in substantially broken-down form, and which also contains a collector chemical, characterised in that the collector chemical comprises a salt formed by reaction of a long-chain fatty acid, and an amine of general formula R¹R²R³N, wherein R¹ represents a group of general formula -C_nH_{2n+1} or -C_n(OH)H_{2n}, where n represents an integer from 1 to 6 inclusive, R² represents a hydrogen atom or a group of general formula -C_mH_{2m+1} or -C_m(OH)H_{2m}, where m represents an integer from 1 to 6 inclusive, and R³ represents a hydrogen atom or a group of general formula -C_pH_{2p+1} or -C_p(OH)H_{2p}, where p represents an integer from 1 to 6 inclusive.
2. A method as claimed in Claim 1, wherein the amine is of general formula R¹R²R³N wherein R¹ represents a group of general formula -C_n(OH)H_{2n}, where n represents an integer from 1 to 6 inclusive, R² represents a hydrogen atom or a group of general formula -C_m(OH)H_{2m}, where m represents an integer from 1 to 6 inclusive, and R³ represents a hydrogen atom or a group of general formula -C_p(OH)H_{2p}, where p represents an integer from 1 to 6 inclusive.
3. A method as claimed in Claim 1, wherein R¹ represents a straight chain group of general formula -C_nH_{2n}-OH where n represents an integer of from 1 to 4 inclusive, R² represents a hydrogen atom or a straight chain group of general formula -C_mH_{m2+1} or -C_mH_{2m}-OH where m represents an integer of from 1 to 4 inclusive, and R³ represents a hydrogen atom or a straight chain group of general formula

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$-C_pH_{2p+1}$ or $-C_pH_{2p}-OH$ where p represents an integer of from 1 to 4 inclusive.

4. A method as claimed in Claim 2 or 3, wherein the
5 amine comprises a trialkanolamine.

5. A method as claimed in Claim 4, wherein the amine
comprises triethanolamine.

10 6. A method as claimed in any preceding claim, wherein
the long-chain fatty acids comprise C₁₂₋₂₂ fatty acids, or C₂₄
44 dicarboxy fatty acids.

15 7. A method as claimed in any preceding claim, wherein
the collector chemical is supplied in liquid form, being
itself a liquid or a component of a liquid composition at
temperatures in the range about 5-25°C, the concentration
of the collector chemical in the liquid being in the range
about 50-100 wt%.

20 8. A method as claimed in Claim 7, wherein said chemical
collector is a component of a liquid composition which
also comprises a fluidiser component which acts to help
keep the composition in liquid form at ambient
25 temperatures.

9. A method as claimed in Claim 8, wherein the fluidiser
component is selected is a polyhydric alcohol or a
polyoxyalkylene glycol.

30 10. A method as claimed in any preceding claim, wherein
the aqueous medium also contains a dispersant.

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11. A method as claimed in Claim 10, wherein the dispersant comprises an ester derived from an ethylene oxide/propylene oxide co-polymer and a C₁₂₋₂₂ fatty acid.

5 12. A method as claimed in Claim 11, wherein the dispersant also comprises an alkyl aryl sulphonate.

10 13. A method as claimed in Claim 10, 11 or 12, wherein the collector chemical and the dispersant are comprised in a single composition, which is added to the paper products at the pulping stage and/or the deinking stage.

15 14. A method as claimed in Claim 10, 11 or 12, wherein the dispersant is added to the paper products at the pulping stage and the collector chemical is added at the deinking stage.

20 15. A collector chemical, or composition containing a collector chemical, per se, as defined in any preceding claim.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 91/00434

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 D21C5/02

II. FIELDS SEARCHED

Classification System	Minimum Documentation Searched ⁷	Classification Symbols
Int.C1. 5	D21C	

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB,A,2121071 (FERGUSON AND MENZIES LTD.) 14 December 1983 see page 1, lines 85 - 123; claims 1-5, 8 ---	1-3, 6-9, 15
X	EP,A,13758 (HENKEL KG) 06 August 1980 see the whole document ---	1-3, 6, 10, 11, 15
A	US,A,4013505 (C. BALCAR ET AL.) 22 March 1977 see column 4, line 54 - column 5, line 63; claims 1-3 ---	1-3, 6, 10-13, 15

¹⁰ Special categories of cited documents :¹⁰

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¹¹ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention¹² document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step¹³ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.¹⁴ document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

24 JUNE 1991

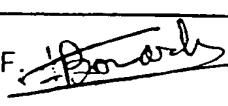
Date of Mailing of this International Search Report

12.07.91

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

BERNARDO NORIEGA F. 

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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